Euro-Mediterr J Environ Integr (2017) 2:8
DOI 10.1007/s41207-017-0017-x

ORIGINAL PAPER

Study of the degradation of a toxic dye by the catalytic system ($H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$)/H_2O_2

Abir Tabaï[1] · Ouahiba Bechiri[1] · Mostefa Abbessi[1]

Received: 5 July 2016 / Accepted: 9 February 2017 / Published online: 21 March 2017

Abstract In this work, the oxidation of an azo dye (Acid Yellow 99) by H_2O_2 in aqueous solution with the Dawson-type heteropolyanion [$H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$] acting as a catalyst was studied. The effects of different parameters—the initial pH, the initial H_2O_2 concentration, the mass of the catalyst, and the initial dye concentration—on the oxidation of the dye were investigated. The optimal conditions that led to maximum decolorization were found to be: pH 3, catalyst mass = 0.05 g, and $[H_2O_2]_0 = 0.03$ mM for an initial dye concentration of 30 mg L^{-1}.

Keywords Dawson-type heteropolyanions · Acid Yellow 99 · Decolorization · Catalytic oxidation

Introduction

The textile industry's production of dyestuffs creates large volumes of waste water. The World Bank estimates that 17–20% of all industrial water pollution emanates from textile dyeing and treatment processes (Kant 2012). There are serious concerns about the discharge of dye-contaminated waste waters into the environment from both aesthetic and environmental perspectives; the color of the dye is often visible in the waste water, even at concentrations as low as 1 mg L^{-1} (Fernández et al. 2004).

✉ Ouahiba Bechiri
bechirio@yahoo.fr

[1] Laboratory of Environmental Engineering, Department of Process Engineering, Faculty of Engineering, University of Annaba, P.O. Box 12, 23000 Annaba, Algeria

Acid Yellow 99 (AY99) is an anionic dye used in the paint, printing, and textile industries. It is appreciated for its color fastness and weather stability, and is used to dye nylon, wool, and silk (Elwakeel et al. 2016). However, AY99 can cause hard skin and eye irritation (Elwakeel et al. 2016). In addition, the inhalation of Acid Yellow 99 may irritate the respiratory tract, and its ingestion causes irritation to the gastrointestinal tract (Elwakeel et al. 2016).

Various physical and chemical treatment processes have been used for dyes in waste water. Among the methods applied to AY99 is decolorization, such as adsorption with coir pith. It was found that 1 g of coir pith can adsorb 442.13 mg of AY99. This adsorption process is found to be pH dependent; the optimum pH value for the process is 2.0, and it follows the Langmuir–Freundlich dual isotherm model (Khan et al. 2011).

The adsorption of AY99 onto dodecylethyldimethylammonium (DEDMA)-sepiolite was investigated in aqueous solution (Ozcan and Ozcan 2008). The photocatalytic decolorization of Acid Yellow 99 solutions under the action of solar radiation using ZnO as a photocatalyst has also been studied (Pitchaimuthu et al. 2014). 98.0% decolorization of an AY99 dye solution was achieved within 180 min using this method. The extraction of AY99 by a liquid surfactant membrane was also studied (Bahloul et al. 2014). The membrane consisted of the surfactant SPAN 80 (sorbitan monooleate) and the extractant Aliquat 366. Cyclohexane was used as the thinner, and sulfuric acid as the internal phase. Extraction yields of 99.09–99.12% were obtained experimentally.

Recently, the development of inexpensive water remediation technologies has attracted considerable interest (Kant 2012). One such method may be the oxidation of organic textile dyes by hydrogen peroxide using polyoxometalates (POMs) as catalysts. H_2O_2 is an

environmentally benign oxidant that is cheap, readily available, and produces a nontoxic substance—water—during oxidation (Qiu and Liu 2005). Polyoxometalates (POMs) are a diverse class of anionic metal oxide clusters that contain early transition metals in their highest oxidation states (Pope 1983). These compounds, which are minerals, are generally easy to synthesize from relatively environmentally friendly simple reagents. Many POMs are known to be effective catalysts of the oxidation of a wide range of organic compounds. They are also potentially applicable in the photodegradation, degradation, and mineralization of organic pollutants in waste water (Hu and Burns 2002; Troupis et al. 2009; Lee and Sedlak 2009; Bechiri et al. 2013). Dawson-type heteropolyanions (Fig. 1) are a family of interesting and selective recyclable POM catalysts (Gustavo et al. 2008).

Given the discussion above, we decided to study the catalytic oxidation of Acid Yellow 99 in contaminated water by H_2O_2 using the recyclable Dawson-type iron-substituted heteropolyanion $H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$ ($P_2W_{12}Mo_6$ Fe^{3+}) as catalyst. We examined how parameters such as the initial pH, the initial H_2O_2 concentration, the mass of the catalyst, and the initial dye concentration affect the oxidation of AY99, and the results are reported in the present paper.

Experimental section

Reagents

The catalyst $HFe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$ was prepared starting from $H_6P_2W_{12}Mo_6O_{62}.24H_2O$ according to the protocol described in Bechiri et al. (2014).

The heteropolyanion precursor $H_6P_2W_{12}Mo_6O_{62}$ $24H_2O$ was synthesized according to the procedure outlined in Ciabrini et al. (1983). The purity of the synthesized heteropolyanions was confirmed by ^{31}P NMR spectroscopy (Bechiri et al. 2014).

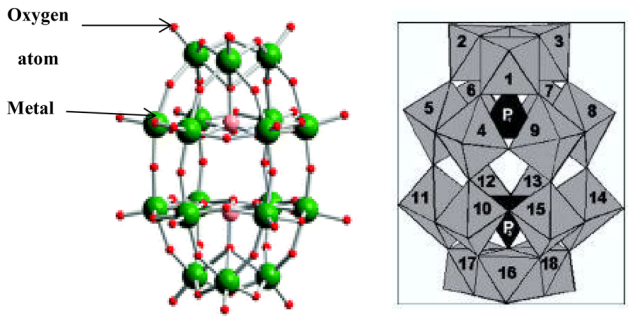


Fig. 1 Polyhedral representation of the Dawson structure of polyanion (Pope 1983; Carraro and Gross 2014)

The anionic dye Acid Yellow 99 was supplied by Sigma–Aldrich (St. Louis, MO, USA). The chemical structure and other characteristics of this dye are shown in Table 1.

H_2O_2 35% (w/w) was obtained from Merck (Darmstadt, Germany).

NaOH, H_2SO_4, and ammonium heptamolybdate $(NH_4)_6Mo_7{\cdot}4H_2O$ were procured from Sigma–Aldrich. Potassium iodide (KI) was supplied by Riedel-de Haën (Seelze, Germany).

Procedure and analysis

The experiments were performed in a 500-mL batch reactor. Various solutions of AY99 were prepared at different concentrations, which were then homogenized by stirring until the dye was completely dissolved. The pH was adjusted using 0.1 N H_2SO_4 or NaOH. In all of the experiments, 100 mL of a 30 mg L^{-1} dye solution containing the appropriate quantities of catalyst and H_2O_2 were magnetically stirred at room temperature. The decrease in the concentration of AY99 was monitored by a model 6705 Jenway UV visible spectrophotometer (Cole-Parmer, London, UK); the wavelength of maximum absorbance λ_{max} was 450 nm (Pitchaimuthu et al. 2014).

Wavelength and bandwidth resolutions were 1 and 0.5 nm. The cell used during the experiments was made of 1-cm-thick quartz.

The concentration of H_2O_2 was determined spectrophotometrically using potassium iodide and ammonuim heptamolybdate salt as the catalyst (Kormann et al. 1988).

The oxidation of AY99 by H_2O_2 using $H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$ as catalyst was studied by monitoring the effects of varying the initial pH of the solution, the H_2O_2 concentration, the mass of the catalyst, and the dye concentration on the oxidation reaction. The oxidation efficiency (i.e., the discolorization efficiency) was determined via the equation (Sasmaz et al. 2011)

$$DE = [(C_i - C_f)/C_i] \times 100, \quad (1)$$

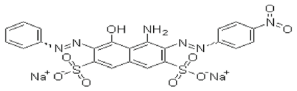
where DE is the discolorization efficiency, C_i is the initial dye concentration, and C_f is the final dye concentration.

Results and discussion

Effect of the solution pH

The effect of pH on the discolorization efficiency was investigated by varying the pH from 3 to 8. At a strongly acidic pH (<3), there is a risk that the catalyst will dimerize, while the catalyst is likely to deteriorate when the pH is above 8 (Bechiri et al. 2012).

Table 1 Physical and chemical properties of the dye AY99

Molecular formula	$C_{16}H_{13}N_4NaO_8S$
Chemical structure	
Synonym	Acid Yellow GR, Acid Yellow GRN, Acid Yellow 3KM
Molecular weight	444.35 g/mol
Colour Index Number	13900

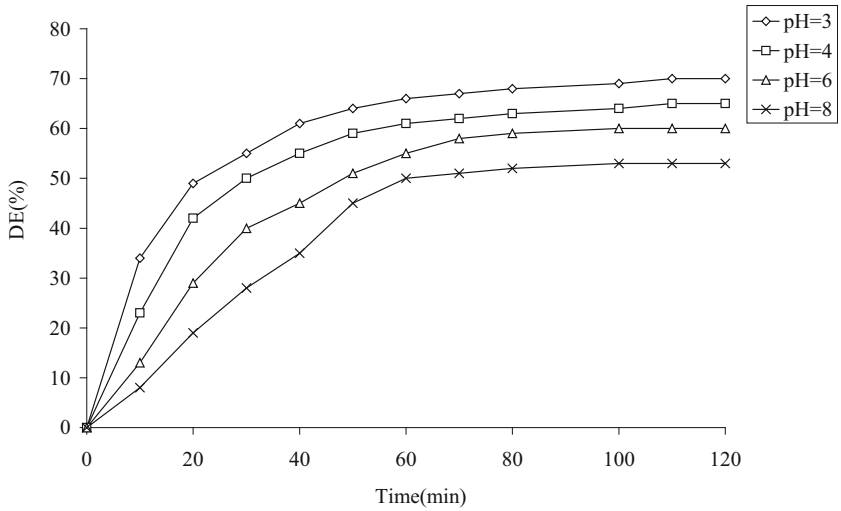


Fig. 2 Effect of solution pH on AY99 oxidation (C_0 = 30 mg/L; $[H_2O_2] = 0.06$ mM; $[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}, 22H_2O] = 0.23$ mM)

The results presented in Fig. 2 show that the optimum pH value for the oxidation of AY99 by H_2O_2 using the iron-substituted Wells–Dawson-type heteropolyanion $HFe_{2.5}P_2W_{12}Mo_6O_{62}.22H_2O$ as catalyst is 3. This result agrees with those reported in Bechiri et al. (2014), in which the oxidation of an azo dye (methyl violet) by H_2O_2 in aqueous solution using a Dawson-type heteropolyanion ($HFe_{2.5}P_2W_{12}Mo_6O_{62}.22H_2O$) as catalyst was studied; in that work, the optimum pH was found to be about 3.

This result can be explained by the enhanced stability of the catalyst at this pH (Bechiri et al. 2013). It has also been shown that the catalytic efficiency of the Fe^{3+}/H_2O_2 system during the oxidation of organic dyes is highest at pH 3 (Strukul 1992). H_2O_2 molecules are unstable in alkaline solution, so dye degradation decreases in alkaline solution (Gould et al. 2005).

Possible reaction mechanism

Figure 3 shows the evolution of the H_2O_2 concentration during the oxidation catalyzed by ($HFe_{2.5}P_2W_{12}Mo_6O_{62}.22H_2O$)/$H_2O_2$. The H_2O_2 concentration decreases during the oxidation process, suggesting that $HFe_{2.5}P_2W_{12}Mo_6O_{62}.22H_2O$ catalyzes the decomposition of H_2O_2. The action of H_2O_2 on the Fe^{2+} complex leads to the generation of hydroxyl radicals (OH·). These hydroxyl radicals degrade the dye (Bechiri et al. 2013).

Therefore, we can propose the following mechanism:

$$(P_2W_{12}Mo_6)Fe^{3+} + H_2O_2 \rightarrow (P_2W_{12}Mo_6)Fe^{2+} + HO_2^{\cdot} \quad (2)$$

$$(P_2W_{12}Mo_6)Fe^{2+} + H_2O_2 \rightarrow (P_2W_{12}Mo_6)Fe^{3+} + 2OH^{\cdot} \quad (3)$$

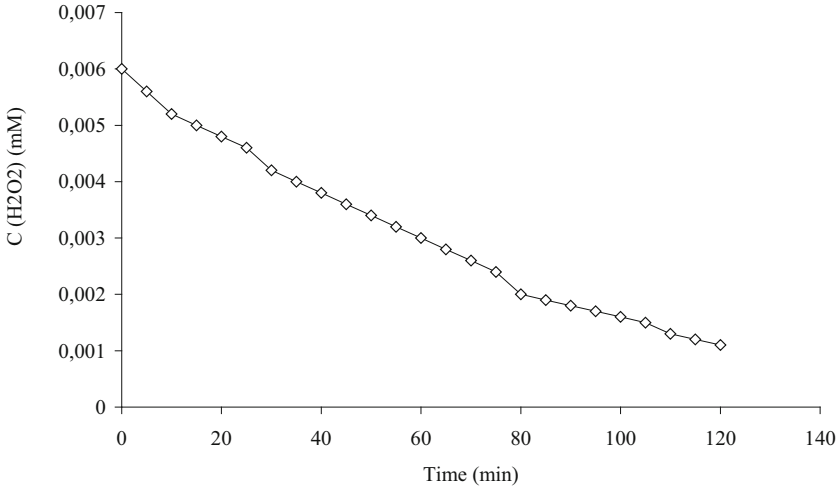


Fig. 3 Evolution of the H_2O_2 concentration during the oxidation of AY99 as catalyzed by ($H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}$, $22H_2O$)/H_2O_2 (pH 3; catalyst mass = 0.05 g; $[H_2O_2]$ = 0.06 mM)

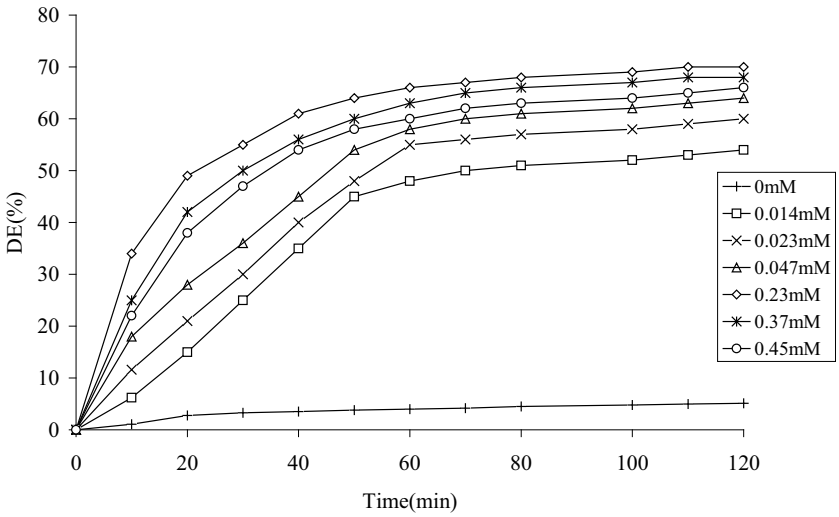


Fig. 4 Effect of the catalyst concentration on AY99 oxidation (pH 3; C_0 = 30 mg L^{-1}; $[H_2O_2]$ = 0.06 mM)

Effect of the catalyst concentration

The mass of the catalyst is a critical parameter in catalytic oxidation processes (Bechiri et al. 2012). Thus, the effect of varying the catalyst mass on the AY99 decolorization efficiency was investigated in this work by varying the concentration of $P_2W_{12}Mo_6Fe^{3+}$ from 0 to 0.45 mM. The results are shown in Fig. 4. The concentration of hydrogen peroxide was fixed at 0.006 mM and the AY99 concentration was 30 mg/L.

It is clear from the results that the AY99 decolorization efficiency increases as the catalyst mass is increased up to a certain level. This is due to the fact that $P_2W_{12}Mo_6Fe^{3+}$ plays a very important role in the decomposition of H_2O_2 into hydroxyl radicals. The low degradation capacity at low $P_2W_{12}Mo_6$ Fe^{3+} concentrations is probably due to the relative scarcity of OH· radicals. As the concentration of the catalyst increases, the number of radicals increases, increasing the decolorization efficiency; however, when the catalyst concentration exceeds a certain value, the decolorization efficiency begins to decrease. This decrease in AY99 decolorization efficiency at large catalyst concentrations can be explained by the occurrence of reaction (4) below, which becomes competitive with the AY99 oxidation reaction at high $P_2W_{12}Mo_6Fe^{3+}$ concentrations:

$$P_2W_{12}Mo_6Fe^{2+} + OH^{\cdot} \rightarrow P_2W_{12}Mo_6Fe^{3+} + OH^{-}. \quad (4)$$

Consequently, a $P_2W_{12}Mo_6Fe^{3+}$ concentration of 0.23 mM was chosen for AY99 oxidation.

Effect of the initial H_2O_2 concentration

The initial H_2O_2 concentration is an important influence on the degradation of AY99 and thus the decolorization efficiency. The effect of this parameter was studied by varying

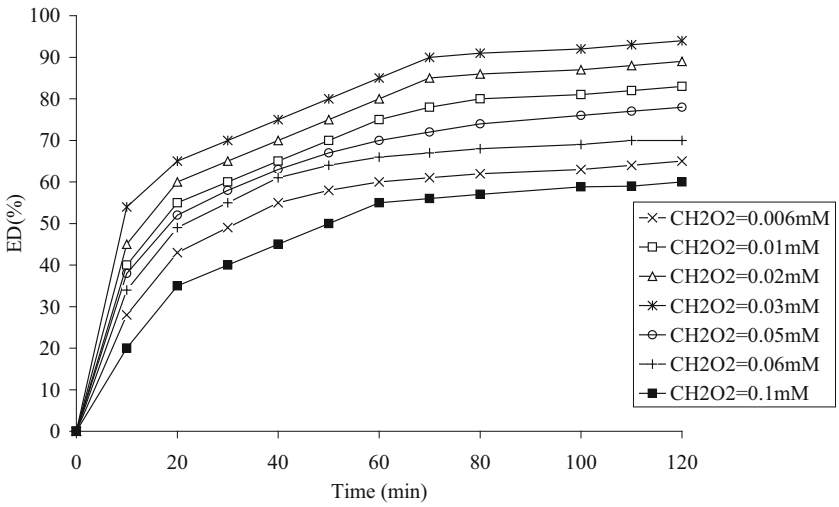


Fig. 5 Effect of the initial H_2O_2 concentration on AY99 oxidation ($[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}, 22H_2O] = 0.23$ mM; pH 3; $C_0 = 30$ mg L^{-1})

the initial H_2O_2 concentration from 0.006 to 0.1 mM under the following optimal conditions: pH 3, [NBB] = 30 mg L^{-1}, [catalyst] = 0.23 mM.

Based on the results shown in Fig. 5, the optimal initial H_2O_2 concentration for the degradation of 30 mg/L AY99 is about 0.03 mM.

The activation of hydrogen peroxide by homogeneous catalysts has been attributed to the formation of highly active hydroxyl radicals (Anipsitakis and Dionysiou 2004). A highly concentrated H_2O_2 solution (0.03–0.1 mM) presents self-quenching of OH· radicals and the formation of hydroperoxyl radicals (HO_2·). Although HO_2· is an effective oxidant, it is a less effective oxidant than OH·, so the AY99 decolorization efficiency drops when the concentration of H_2O_2 exceeds a threshold value (Liu et al. 2005).

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \left(k = 2.7 \times 10^7 \text{mol}^{-1}\text{L s}^{-1}\right) \quad (5)$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \left(k = 0.71 \times 10^{10} \text{mol}^{-1}\text{L s}^{-1}\right) \quad (6)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \left(k = 5.2 \times 10^9 \text{mol}^{-1}\text{L s}^{-1}\right). \quad (7)$$

Effect of the AY99 concentration

From Fig. 6, it is clear that the discolorization efficiency decreases with increasing initial concentration of the dye. This result is in good agreement with results reported in the literature, and can be explained by the fact that increasing the initial dye concentration increases the ratio of AY99 molecules to hydroxyl radicals (as the concentrations of H_2O_2 and the catalyst are fixed), thereby decreasing the discolorization efficiency (Ramirez et al. 2007; Li et al. 2006; Ji et al. 2011).

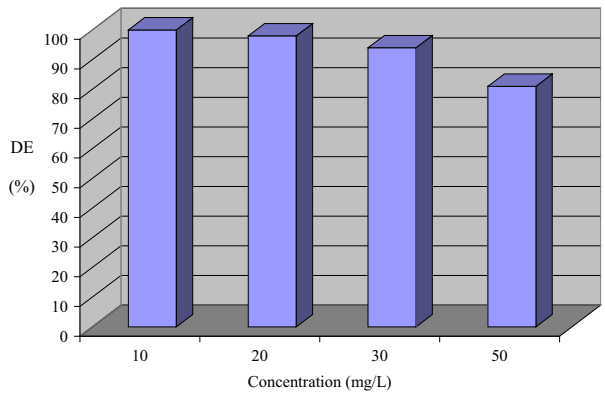


Fig. 6 Effect of the initial dye concentration on AY99 oxidation (pH 3; $[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}, 22H_2O] = 0.23$ mM; $[H_2O_2] = 0.03$ mM)

Monitoring the catalyzed oxidative degradation of AY99 over time using visible spectroscopy

Under the optimal experimental conditions determined above (pH 3; $[H_2O_2] = 0.03$ mM; $C_0 = 30$ mg L^{-1}; $[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}, 22H_2O] = 0.23$ mM; $T = 25$ °C), we used visible spectroscopy to follow the catalyzed oxidative degradation of AY99 over time. The results are depicted in Fig. 7. The figure shows that the catalytic oxidation process is fast: the color of the dye disappears quickly. The azo dye absorbance peak at $\lambda = 450$ nm that was used to monitor the discolorization decreases in intensity over time and disappears completely 60 min after the start of the reaction.

The decrease in this peak is caused by the cleavage of –N=N– bonds due to attack by hydroxyl radicals (Pitchaimuthu et al. 2014).

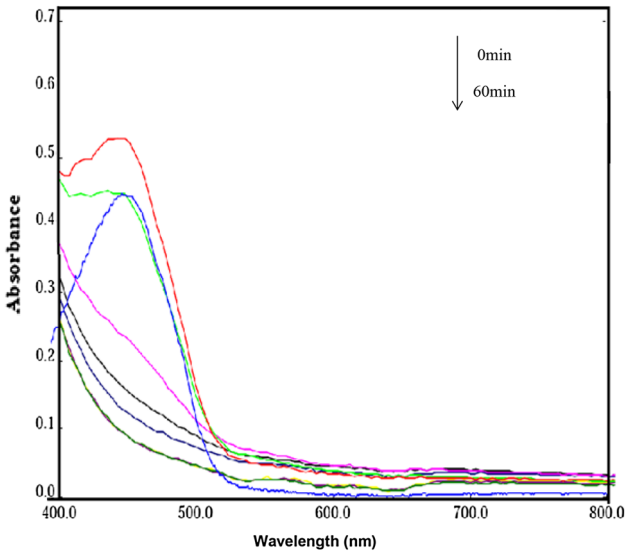


Fig. 7 Application of visible spectroscopy to monitor the catalyzed oxidative degradation of the dye AY99 (pH 3; $[H_{1.5}Fe_{1.5}P_2W_{12}Mo_6O_{61}, 22H_2O] = 0.23$ mM; $[H_2O_2] = 0.03$ mM)

Conclusion

Textile dyes are a large group of organic compounds that can have undesirable effects when released into the environment. In this work, the oxidation of the azo dye AY99 by H_2O_2 in aqueous solution and in the presence of the iron-substituted Dawson-type heteropolyanion catalyst $HFe_{2.5}P_2W_{12}Mo_6O_{62}.22H_2O$ was studied. The optimal parameter values for this oxidation were found to be: initial pH 3; $[H_2O_2]_0 = 0.03$ mM; [catalyst] = 0.23 mM. Note that it is easy to separate and recover (i.e., recycle) this catalyst so that it can be used again. To do this, the catalyst is precipitated as its potassium salt by adding KCl to the solution following complete discolorization. The catalyst can also be separated out by extraction using a liquid surfactant membrane (Bechiri et al. 2008).

Acknowledgements This work was supported by the Engineering Environmental Laboratory of Badji Mokhtar University (Annaba, Algeria), and is dedicated to the late Professor Mostefa Abbessi, God rest his soul.

Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

References

Anipsitakis GP, Dionysiou DD (2004) Radical generation by the interaction of transition metals with common oxidants. Environ Sci Technol 38:3705–3712

Bahloul L, Ismail F, Samar ME, Meradi H (2014) Removal of AY99 from an aqueous solution using an emulsified liquid membrane. Application of Plackett–Burman design. Energy Proced 50:1008–1016

Bechiri O, Ismail F, Abbessi M, Samar MH (2008) Stability of the emulsion (W/O): application to the extraction of a Dawson type heteropolyanion complex in aqueous solution. J Hazard Mate 152:895–902

Bechiri O, Abbessi M, Ouahab L (2012) The oxidation study of methyl orange dye by hydrogen peroxide using Dawson-type heteropolyanions as catalysts. Res Chem Intermed 39:2945–2954

Bechiri O, Abbessi M, Samar ME (2013) Decolorization of organic dye (NBB) using $Fe(III)P_2W_{12}Mo_5/H_2O_2$ system. Desalination Water Treat 51:31–33

Bechiri O, Abbessi M, Belghiche R, Ouahab L (2014) Wells–Dawson polyoxometelates $[HP_2W_{18-n}Mo_nO_{62}]Fe_{2.5}$, xH_2O; n = 0, 6: synthesis, spectroscopic characterization and catalytic application for dyes oxidation. C R Chim 17:135–140

Carraro M, Gross S (2014) Hybrid materials based on the embedding of organically modified transition metal oxoclusters or polyoxometalates into polymers for functional applications: a review. Materials 7:3956–3989

Ciabrini JP, Contant R, Fruchart M (1983) Heteropolyblues: relationship between metal-oxygen-metal bridges and reduction behaviour of octadeca(molybdotungsto)diphosphate anions. Polyhedron 2:1229–1233

Elwakeel KZ, El-Bindary A, El-Sonbati AZ, HawasA R (2016) Adsorption of toxic acidic dye from aqueous solution onto diethylenetriamine functionalized magnetic glycidyl methacrylate-*N*,*N*′-methylenebisacrylamide. RSC Adv 6:3350–3361

Fernández J, Kiwi J, Baeza J, Freer J, Lizama C, Mansilla HD (2004) Orange II photocatalysis on immobilised TiO_2: effect of the pH and H_2O_2. Appl Catal B 48:205–211

Gould DM, Spiro M, Griffith WP (2005) Mechanism of bleaching by peroxides: part 7. The pH dependence of the oxometalate catalysed bleaching of methyl orange. J Mol Cat A Chem 242:176–181

Gustavo R, Bennardi DO, Autino J, Baronetti G, Thomas H (2008) A simple and mild acylation of alcohols, phenols, amines, and thiols with a reusable heteropoly acid catalyst ($H_6P_2W_{18}O_{62}.24H_2O$). Eur J Chem 5:641–647

Hu J, Burns RC (2002) Homogeneous-phase catalytic H_2O_2 oxidation of isobutyraldehyde using Keggin, Dawson and transition metal-substituted lacunary heteropolyanions. J Mol Cat A Chem 184:451–464

Ji F, Li C, Zhang J, Deng L (2011) Efficient decolorization of dye pollutants with LiFe $(WO_4)_2$ as a reusable heterogeneous Fenton-like catalyst. Desalination 269:284–290

Kant R (2012) Textile dyeing industry an environmental hazard. Nat Sci 1:22–26

Khan MM, Ray M, Guha AK (2011) Mechanistic studies on the binding of Acid Yellow 99 on coir pith. Bioresour Technol 102:2394–2399

Kormann C, Bahnemann DW, Hoffmann MR (1988) Photocatalytic production of H_2O_2 and organic peroxides in aqueous suspensions of TiO_2, ZnO, and desert sand. Environ Sci Technol 22:798–806

Lee DL, Sedlak C (2009) A novel homogeneous Fenton-like system with Fe(III)–phosphotungstate for oxidation of organic compounds at neutral pH values. J Mol Catal A Chem 311:1–6

Li G, Qu J, Zhang X, Liu H, Liu H (2006) Electrochemically assisted photocatalytic degradation of Orange II: influence of initial pH values. J Mol Catal A Chem 259:238–244

Liu RM, Chen SH, Hung MY, Hsu CS, Lai JY (2005) Fe III supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution. Chemosphere 59:117–125

Ozcan S, Ozcan A (2008) Adsorption of Acid Yellow 99 onto DEDMA-sepiolite from aqueous solutions. Int J Environ Pollut 34:308–324

Pitchaimuthu S, Subramanian R, Nagarathinam K, Ponnusamy V (2014) Enhanced photocatalytic activity of titanium dioxide by β-cyclodextrin in decoloration of Acid Yellow 99 dye. Desalin Water Treat 52:3392–3402

Pope MT (1983) Heteropoly and isopoly oxometalates. Springer, New York

QiuZ HeY, LiuX YuS (2005) Catalytic oxidation of the dye wastewater with hydrogen peroxide. Chem Eng Process 44:1013–1017

Ramirez HJ, Costa CA, Madeira M, Mata G, Vicente MA, Rojas-Cervantes ML, Lopez-Peinado AJ, Martin-Aranda RM (2007) Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay. Appl Catal B 71:44–56

Şaşmaz JS, Gedikli S, Aytar P, Güngörmedi G, Evrim AÇ, Ünal HA, Kolankaya N (2011) Decolorization potential of some reactive dyes with crude laccase and laccase-mediated system. Appl Biochem Biotechnol 163:346–361

Strukul G (1992) Catalytic oxidations with hydrogen peroxide as oxidant. Kluwer Academic, Dordrecht, The Netherlands

Troupis A, Triantis TM, Gkika E, Hiskia A, Papaconstantinou E (2009) Photocatalytic: reductive–oxidative degradation of Acid Orange 7 by polyoxometalates. Appl Catal B Environ 86:98–107